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(54) Title: SILVER ALLOY COMPOSITIONS

(57) Abstract

Firescale resistant bright silver alloys are provided exhibiting lack of significant firescale formation under normal casting an hot working conditions and a comparatively high copper content. A deoxidizing additive (silicon) provides the facility of high copper content without significant firescale production in the absence of the usual aggressive deoxidizers such as zinc. Germanium is alloyed in the composition to provide work hardening characteristics. Copper proportions of from 2.5 % by weight to 19.5 % by weight are attained. Compositions of silver, copper, silicon and germanium are disclosed, together with compositions modified by the addition of indium, boron or tin.

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SILVER ALLOY COMPOSITIONS

FIELD OF THE INVENTION

This invention relates to silver alloy compositions.

This invention has particular reference to sterling silver alloy compositions of silver content of at least 92.5% for jewellery, flatware, coinage and other applications where a work hardening alloy is required and for illustrative purposes reference will be made to this application. However, it is to be understood that this invention could be used to produce other types of silver alloys suitable for use as for example, electrical contacts or the like.

BACKGROUND OF THE INVENTION

In general, silver as a material for the production of silver jewellery, certain coinage and the like is specified to be sterling silver comprising at least 925 parts per thousand by weight fine silver and is specified as ".925 silver". .925 silver accordingly typically comprises an alloy 92.5% by weight silver, generally alloyed with copper for hardness traces of other metals as additives or impurities.

Conventional silver alloys of the .925 type have several disadvantages in manufacturing jewellery and other materials engineering contexts. Principal limitations include a characteristic firescale formation attributed to oxidation of copper and other metals at the surface of cast or hot worked pieces, and poor work hardening characteristics relative to traditional .925 silvers.

Several formulations have been proposed to overcome one or the other of the aforementioned disadvantages. United States Patent Nos. 5039479 and 4973446 disclose alloys of silver and master alloys for the production of such silver alloys having superior qualities over conventional alloys, and including, in addition to silver, controlled amounts of copper and zinc, together with minor amounts of tin, indium, boron and silicon.

The compositions exhibit reduced porosity, grain size and fire scale production, and have acquired wide utilization in silver jewellery production. It is presumed but not established that the addition of zinc to such compositions provides at least a degree of antioxidant properties to the compositions when hot worked and improves colour, thus allegedly limiting the formation of copper oxide based fire scale, and reducing silver and copper oxide formation resulting in formation of pores in the cast or recast alloys. Silicon appears also to function as an antioxidant, and apparently reduces firescale formation.

A disadvantage of the hereinbefore described firescale resisting alloys is that the alloys exhibit poor work hardening qualities thus not achieving the mechanical strength of traditional worked .925 silver goods. A further disadvantage of the prior art alloys is that formulations in accordance therewith are generally limited to modest copper content, thus reducing the potential as-cast hardness.

International Patent Application No. PCT/AU94/00351 discloses improved .925 silver alloys exhibiting firescale resistance and work hardening characteristics comparable to traditional .925 silvers. Again, the alloys are characterised by a relatively low copper content of about 0.5 by weight, about 0.02 - 7% by weight of a firescale resisting additive selected from one or a mixture of zinc and silicon, and about 0.01 - 2.5% by weight germanium.

However, in some applications a high copper alloy is desired for its hardness. Such high copper alloys were generally regarded as firescale prone due to elevated levels of copper oxide being formed at the metal surface. It has unexpectedly been discovered by the applicant that such high copper alloys can be formulated to exhibit firescale resistance.

DISCLOSURE OF THE INVENTION

The present invention aims to provide high copper silver

alloy compositions which substantially alleviate at least one of the foregoing disadvantages. A further object of the present invention is to provide high copper silver alloys having the desirable properties of reduced fire scale, reduced porosity and oxide formation and reduced grain size relative to traditional sterling silver alloys whilst providing improved work hardening performance over the current firescale resistant alloys. Other objects and advantages of this invention will hereinafter become apparent.

With the foregoing and other objects in view, this invention in one aspect resides broadly in silver alloy compositions comprising:-

2.5 - 19.5% by weight copper;
0.02 - 2% by weight of silicon;
0.01 - 3.3% by weight germanium, and
silver to 100%.

Like the prior art firescale resistant bright sterling alloys, alloys in accordance with the present invention do not exhibit significant firescale under normal casting and hot working conditions. Unlike the previous bright sterling alloys, the present alloys are comparatively high in copper content and are accordingly harder as cast and with working. As it is accepted belief that firescale is a copper oxide and that high copper alloys are inherently firescale prone, to create a high copper content, firescale free sterling silver is quite contrary to expectation.

In particular it is unexpectedly found that the choice of deoxidizing additive (silicon) provides the facility of high copper content without significant firescale production, whereas the more common aggressive deoxidizers such as zinc do not. Firescale resistance is of particular importance for hot working for hardness and in this context the use of germanium as an alloying agent provides alloys which are both firescale resistant and work hardenable, and which in any

case are harder than prior art alloys due to their elevated copper content.

Preferably, the alloy contains a proportion of silver required for the graded application to which the alloy is to be put, such as .925 silver, that is at least 92.5% by weight, for sterling silver applications and at least 90% by weight for coinage.

The copper content of the alloys may be selected to provide a desirable as-cast hardness of the product alloys. Below about 2.5% by weight, the alloy does not attain an appreciable hardness benefit. Over 19.5% copper, the compositions do not exhibit the required firescale resistance, at the maximum practical usage of silicon deoxidizer. Preferably, the copper content of the alloy is in the region of 6 to 16% by weight.

The germanium content of the alloy results in alloys having work hardening characteristics of a kind with those exhibited by conventional .925 silver alloys, together with the firescale resistance of the hereinbefore described firescale resistant alloys. In general, it has been determined that amounts of germanium in the alloy of from about 0.04 to 2.0% by weight provide modified work hardening properties relative to alloys of the firescale resistant kind not including germanium. However, it is noted that the hardening performance is not linear with increasing germanium nor is the hardening linear with degree of work.

The alloys of the present invention may also include rheology modifying and other additives to aid in improving the castability and/or wetting performance of the molten alloy. As described hereinafter, the modified alloys of the present invention are described in terms of weight percentage of additive added to the defined composition of the aforementioned alloys of the present invention.

For example, about 0.0 to 3.5% by weight of a modifying additive selected from one or a mixture of indium and boron

may be advantageously added to the alloy to provide grain refinement and/or reduce surface tension, thereby providing greater wettability of the molten alloy. Where used, preferably the amount of boron utilized in the composition is from about 0 to 2% by weight boron and/or about 0 to 1.5% by weight indium.

Accordingly, in a further aspect this invention resides in silver alloy compositions comprising 0.0 to 3.5% by weight of a modifying additive selected from one or a mixture of indium and boron alloyed with a composition selected from alloys comprising:-

2.5 - 19.5% by weight copper;
0.02 - 2% by weight of silicon;
0.01 - 3.3% by weight germanium, and
silver to 100%.

Of particular utility in alloys of the present invention is the addition of tin, used up to about 6% by weight of the compositions as defined. Accordingly, in a further aspect this invention resides broadly in silver alloy compositions comprising tin in an amount of 0-6% by weight alloyed with a composition selected from alloys comprising:-

2.5 - 19.5% by weight copper;
0.02 - 2% by weight of silicon;
0.01 - 3.3% by weight germanium, and
silver to 100%.

The selection of alloys have particular application to jewellery manufacture and plate work and in a further aspect this invention relates to a method of producing cast and hot worked jewellery and plate including working an alloy comprising:

2.5 - 19.5% by weight copper;
0.02 - 2% by weight of silicon;
0.01 - 3.3% by weight germanium, and
silver to 100%.

In the production of alloys in accordance with the

present invention, the alloys are generally worked up by the melt addition of a master alloy to fine silver. Accordingly, in a further aspect this invention resides broadly in a method of producing silver alloy compositions comprising alloying to at least 80 wt% silver with a master alloy comprising:

43.0 - 99.85% by weight copper;

0.1 - 44.3% by weight silicon, and

0.05 - 56.7% by weight germanium.

The invention will be further described with reference to the following example.

EXAMPLE 1

Three alloys were prepared in accordance with the compositions of Table 1:

TABLE I - ALLOYS

	B16	B20	830*
Ag	92.5	92.5	83
Cu	7.0	6.8	16.5
Si	.2	.3	.2
Ge	.3	.2	.3
Sn		.2	

* 830 is a standard grade

Amounts of alloying constituents are given as percentages by weight of alloy. The compositions were then tested for hardness, as cast, after rolling to reduce thickness of a cast ingot by 50% and 75% of its original dimension, and annealed. The hardness characteristics of the alloys is given in Table 2, the tests being done in triplicate:

TABLE II - HARDNESS HV_{10}

ALLOY	AS CAST	50% ROLLED	75% ROLLED	ANNEALED
B16	86.9	164	170	73.3
	88.4	162	180	73.6
	92.4	163	181	73.6
B20	78.8	151	167	71
	73.6	151	161	70.2
	76.3	145	168	70.7

Alloys in accordance with the above embodiments resist production of firescale under normal casting and hot working conditions. The alloys are relatively high in copper content and are accordingly harder as cast and with working. As it is accepted belief that firescale is a copper oxide, to create a high copper content, firescale free sterling silver is quite contrary to expectation. The alloys achieve their object with fewer alloying components than is generally accepted to be desirable, fewer components providing the added advantage of a more stable grain structure.

It will of course be realised that while the above has been given by way of illustrative example of this invention, all such and other modifications and variations thereto as would be apparent to persons skilled in the art are deemed to fall within the broad scope and ambit of this invention as defined in the claims appended hereto.

CLAIMS:-

1. Silver alloy compositions comprising:-
   2.5 - 19.5% by weight copper;
   0.02 - 2% by weight of silicon;
   0.01 - 3.3% by weight germanium, and
   silver to 100%.

2. Silver alloy compositions according to Claim 1, wherein the silver content of the alloy is at least 83.0% by weight.

3. Silver alloy compositions according to Claim 2, wherein the silver content of the alloy is at least 92.5% by weight.

4. Silver alloy compositions according to Claim 1, wherein the copper content of the alloy is in the region of 6 to 16% by weight.

5. Silver alloy compositions in accordance with any one of the preceding Claims, wherein the germanium content of the alloy is from about 0.04 to 2.0% by weight.

6. Silver alloy compositions comprising an alloy in accordance with any one of Claims 1 to 5 and having alloyed therewith a modifying additive in an amount of 0.0 to 3.5% by weight of the original composition, said modifying additive being selected from one or a mixture of indium and boron.

7. Silver alloy compositions according to Claim 6, wherein said boron content is from about 0 to 2% by weight and said indium content is about 0 to 1.5% by weight.

8. Silver alloy compositions comprising an alloy in accordance with any one of Claims 1 to 5 and having alloyed therewith tin in an amount of 0.0 to 6.0% by weight of the compositions as defined.

9. A silver alloy composition comprising:-
   92.5 wt% silver
   7.0 wt% copper
   0.2 wt% silicon
   0.3 wt% germanium

10. A silver alloy composition comprising:-
   92.5 wt% silver
   6.8 wt% copper
   0.3 wt% silicon
   0.2 wt% germanium
   0.2 wt% tin

11. A silver alloy composition comprising:-
   83.0 wt% silver
   16.5 wt% copper
   0.2 wt% silicon
   0.3 wt% germanium

12. A method of producing silver alloy compositions comprising alloying to at least 80 wt% silver with a master alloy comprising:
   43.0 - 99.85% by weight copper;
   0.1 - 44.3% by weight silicon, and
   0.05 - 56.7% by weight germanium.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/AU 96/00019

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl[6]: C22C 5/06, 5/08, 1/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC : C22C 5/06, 5/08, 1/03, 9/00, 9/10, 28/00, 30/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU : IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT : IPC as above and (Cu or copper) and (Si or silicon) and (Ge or germanium)
JAPIO : as above

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 95/14112 (APECS INVESTMENT CASTINGS P TY LTD) 26 May 1995 see claims 1, 7, 13	1-3, 5-8, 13
X	Patent Abstracts of Japan, M192, page 156, JP 57-187195 A (TOKURIKI HONTEN KK) 17 November 1982 see Abstract	1-5, 9, 11
A	US 5039479 A (BERNHARD et al) 13 August 1991 Abstract, column 3 line 55 - column 4 line 11, claims	1-12

[X] Further documents are listed in the continuation of Box C

[X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search	Date of mailing of the international search report
27 March 1996	3RD APRIL 1996.

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C (Continuation)	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2255348 A (METHALEUROP RECHERCHE) 04 November 1992 Abstract, page 1 paragraph 4 - page 3 paragraph 2	1-5
A	US 4124380 A (YOUDELIS) 07 November 1978 Abstract, column 1 lines 56-67, column 3 lines 19-34	1-5, 8
A	Patent Abstracts of Japan, C39, page 165, JP 55-138042 A, 28 October 1980 Abstract	1-5, 8

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No.
PCT/AU 96/00019

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
WO	9514112	AU	70629/94				
GB	2255348	DE	4213897	FR	2675817		
US	4124380	CA	1082492	IN	150271		
JP	55138042	CA	1129680	DE	2924238	FR	2428904
		GB	2029446	US	4279649	NL	7904752
		SE	7905304				

END OF ANNEX